

BEST AVAILABLE COPY

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)



सत्यमेव जयते

REC'D 29 OCT 2004

WIPO

PCT



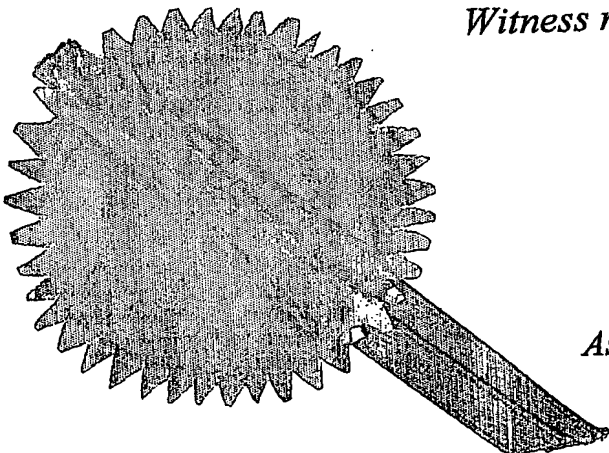
INTELLECTUAL  
PROPERTY INDIA

GOVERNMENT OF INDIA  
MINISTRY OF COMMERCE & INDUSTRY  
PATENT OFFICE, DELHI BRANCH  
W - 5, WEST PATEL NAGAR  
NEW DELHI - 110 008.

IN/04/234

*I, the undersigned being an officer duly  
authorized in accordance with the provision of the  
Patent Act, 1970 hereby certify that annexed hereto is  
the true copy of the Application, Provisional and  
Complete Specification filed in connection with  
Application for Patent No.971/Del/2003 dated 06<sup>th</sup>  
August 2003.*

*Witness my hand this 1<sup>st</sup> day of September 2004.*



  
(S.K. PANGASA)

Assistant Controller of Patents & Designs

0971 DEL 03

Ifc - MM

Chemistry  
COSD 5/00

06 AUG 2003

FORM 1

THE PATENTS ACT, 1970

(39 of 1970)

APPLICATION FOR GRANT OF A PATENT OFFICE

[See section 5(2), 7/54 and 135]

Govt. of India Patent Office	
New Delhi	
Received Rs. 3080/-	in cash.
Cheque/M.O. R.P.O.D.D.	
06 AUG 2003	
Vide Entry No. 5086	in the
Register of Valuables	
A. O.	Cashier.

I/We, Department of Science & Technology,  
Technology Bhavan, New Mehrauli Road,  
New Delhi - 110 016,  
India.

2. Hereby declare: -

(a) That I am/we are in possession of an invention titled: -

(b) 'A process for the manufacture of bio-release  
iron-manganese release fertilizer'.

(c) That the Provisional/Complete Specification relating to this invention is filed with this application.

(d) That there is no lawful ground of objection to grant of a Patent to me/us.

3. Further declare that the inventor(s) for the said invention is: -

(a) Dr. (Ms.) Chandrika Varadachari, Director,  
Raman Centre for Applied and Interdisciplinary Sciences,  
(b) 16A Jheel Road,  
Kolkata - 700 075,  
West Bengal, India,  
(c) An Indian Citizen.

(d)

(e)

4. I/We, claim the priority from the application(s) filed in convention countries, particulars of which are as follows: -

(a) NIL

(b) NONE

ORIGINAL

5. I/We state that the said invention is an improvement in or modification of the particulars of which are as follows and of which I/We are the Applicant/Patentee:

- (a) NIL
- (b) NONE

6. I/We state that the application is divided out of my/our application, the particulars of which are given below and pray that this application be deemed to have been filed on ..... under section 16 of the Act:

- (a) NONE
- (b)

7. That I am/We are the assignee or legal representative of the true and first Inventors.

8. That my/our addresses for service in India is as follows:

Head Office

**RAJAGOPALAN & ASSOCIATES**

15, Ganesh Chandra Avenue,

2<sup>nd</sup> Floor, Room No. 6,

Hoare Miller Building,

Calcutta 700 013

Phone No. (91) (33) 237-4875

Fax No. (91) (33) 215-3802

(91) (33) 225-4160

Branch Office

**RAJAGOPALAN & ASSOCIATES**

114F/1D, Selimpur Road,

Ground Floor, Aditya Apartments,

Calcutta 700 031

Phone No. (91) (33) 472-6275

Fax No. (91) (33) 472-6275

(91) (33) 473-0236

9. Following declaration was given by the inventor (s) or applicant (s) in the convention country: -

NONE

I/We the true and first inventors for this invention or the applicant (s) in the convention country declare that the applicant(s) herein is/are my/our assignee or legal representative:

(a) *Chandrika Nandakumar*

(b)

(c)

(d)

(e)


10. That to the best of my/our knowledge, information and belief the fact and matters stated herein are correct and that there is no lawful ground of objection to the grant of patent to me/us on this application.

11. Following are the attachment with the application: -

- ✓ (a) Provisional/~~Complete~~ Specification (3 copies).  
✓ (b) Drawings (3 copies).  
✓ (c) Priority document(s).  
✓ (d) Statement and undertaking on Form ~~3~~..... None.  
(e) Power of Attorney: To follow.  
(f) .....  
(g) .....  
(h) .....  
(i) Fee Rs. 3000/- in Cash/Cheque/Bank Draft bearing No. 008738  
date 04.08.03 on Bank of India Bank.

I/We request that a Patent may be granted to me/us for the said invention.

Dated this 31st day of JULY, 2003



For (Full name & Status)

**R. Saha**  
Advisor/Scientist 'G'  
Deptt. of Science & Technology  
Govt. of India  
Technology Bhawan, New Mehrauli Road,  
New Delhi-110 016

TO  
THE CONTROLLER OF PATENTS,  
THE PATENT OFFICE,  
CALCUTTA/NEW DELHI/MUMBAI/CHENNAI.

THE PATENT ACT, 1970

PROVISIONAL

SPECIFICATION

(SECTION -10)

06 AUG 2003

06 AUG 2003

TITLE

'A PROCESS FOR THE MANUFACTURE OF  
BIO -RELEASE IRON-MANGANESE FERTILIZER'

APPLICANT

TECHNOLOGY INFORMATION, FORECASTING AND ASSESSMENT  
COUNCIL (TIFAC), DEPARTMENT OF SCIENCE & TECHNOLOGY (DST),  
TECHNOLOGY BHAVAN, NEW MEHRAULI ROAD, NEW DELHI 110016.  
AN INDIAN GOVERNMENT ORGANISATION.

ORIGINAL

The following specification particularly describes and ascertains the  
nature of this invention and the manner in which the same is to be performed.

## A PROCESS FOR THE MANUFACTURE OF BIO-RELEASE IRON-MANGANESE FERTILIZER

### Field of invention

This invention relates to a process for the manufacture of a bio-release type of slow-release iron-manganese fertilizer compound wherein these micronutrients are water insoluble but are nevertheless available for plants.

### Background of invention

Iron and manganese fertilizers are widely used in many parts of the world particularly in soils of high pH, such as the black cotton soils. Ferrous sulphate and manganous sulphate are most popularly used for correcting deficiencies of iron and manganese in crops (J.J. Mortvedt, P.M. Giordano & W.L. Lindsay, 1972, *Micronutrients in Agriculture*, Soil Sc. Soc. Am., Madison). Chelated forms of these micronutrients, eg., iron-EDTA, and manganese-EDTA compounds are in use as liquid sprays (V. Saucheli, 1967, *Chemistry and technology of fertilizers*, Reinhold, New York; G.H. Collins, 1955, *Commercial fertilizers*, Mc Graw Hill, New York).

There are, however, several drawbacks in the use of such soluble compounds as fertilizers of iron and manganese, e.g., leaching losses, chemical transformation losses, ground water contamination, etc. This results in excess dosages which are often several times the actual crop uptake, leading to poor fertilizer-use efficiency. Moreover, such wastages also affect the economics of iron and manganese fertilizer, thereby discouraging their usage and causing loss of crop yields.

In an attempt to overcome these short-comings, slow-release fertilizers incorporating iron and manganese have been prepared. One such type are the fertilizers based on phosphate glasses known as frits. Frits are prepared by fusing sodium, potassium or ammonium dihydrogen phosphates together with micronutrient salts at temperatures between 800° and 1400°C and then rapidly quenching the melt to produce a glass (G.J. Roberts 1973, *Am. Ceram. Soc. Bull.* Vol 52, p383; *ibid*, *idem*, Vol 54, p1069; Austrian Patent No 326160 of 1975; US Patent No. 3574591 of 1971; US Patent No 2713536 of 1974).

The major disadvantage of the phosphate glass frits is that the availability of the nutrients is by slow hydrolysis of the glass and is highly dependent on the soil (pH, moisture content, temperature, etc.) and on the crop (rate of growth, physiological factors, variety, etc). Consequently, where nutrient release by hydrolysis does not match plant uptake, the fertilizer is not effective. Moreover, the high temperatures involved in the synthesis of frits together with the corrosive conditions make these materials fairly expensive and unsuitable for use in low value crops.

Another type of phosphate based water insoluble fertilizer is the metaphosphate. Metaphosphates of calcium and potassium together with micronutrients have been proposed (SI Volkovich, 1972, J Appl. Chem (USSR) Vol 45, p2479). A Russian patent (SU 1270148 of 1986) describes the production of mixed metaphosphates based fertilizers produced at 500<sup>o</sup>-880<sup>o</sup>C. Two Indian patents (Nos 172800 of 1990 and 177205 of 1991) describe the process for producing phosphate based zinc and copper fertilizers. The chemistry of zinc and copper phosphate polymerisation and the chemical nature of these fertilizers have also been described (SK Ray, C Varadachari & K Ghosh, 1993, Ind. Eng. Chem. Res. Vol. 32, p. 1218; SK Ray, C Varadachari & K Ghosh, 1997, J. Agric. Food Chem., vol. 45, p. 1447).

Drawbacks in the use of metaphosphates as fertilizers are similar to those with the frits. Metaphosphates may be more insoluble and hydrolyse even slower, producing compounds with very poor nutrient availability. Metaphosphates of the heavy metals are extremely insoluble and of no use as fertilizers.

There is no process available as yet, for producing a water insoluble, iron-manganese fertilizer that will also show good bio-availability of the nutrients and thus provide an effective source of iron and manganese for plants.

#### **Objectives of the invention**

An objective of this invention is to propose a process for the manufacture of a new type of bio-release iron-manganese fertilizer having all the advantages of slow-release fertilizers together with the added benefit of high nutrient availability.

Another objective of this invention is to provide a combined nutrient source of iron and manganese in a single compound since deficiencies of iron and manganese in soils always occur together and, therefore, a fertilizer providing both nutrients would be more beneficial for crop growth.

The third objective of this invention is to provide a bio-release source of magnesium and phosphorus, both of which are essential plant nutrients.

Still another objective of this invention is to propose a process for the manufacture of bio-release iron-manganese fertilizer, which is simple, requires less energy than previous processes and uses only cheap and readily available raw materials.

#### **Description of the invention**

According to this invention, there is provided a process for the preparation of bio-release iron-manganese fertilizers which process comprises heating yellow oxide of iron (goethite), manganese dioxide (pyrolusite), magnesium oxide (magnesia) and phosphoric acid till the resultant mixture forms a thick slurry, further heating to form a iron-manganese-magnesium polyphosphate, mixing the mass with water and a basic compound and finally obtaining a dried powder.

When yellow oxide of iron [goethite or  $\text{FeO}(\text{OH})$ ], pyrolusite ( $\text{MnO}_2$ ) and magnesia ( $\text{MgO}$ ) are heated with phosphoric acid at temperatures of  $100^\circ\text{C}$  and above, reaction occurs to form the dihydrogen phosphates of the metal ions. Removal of free water from the system by heating facilitates the formation of the dihydrogen phosphates. At the end of this reaction period, magnesia and yellow oxide of iron are essentially dissolved in the acid but a fraction of the pyrolusite remains unreacted. The slurry containing the dihydrogen phosphates, when heated at temperatures above  $170^\circ\text{C}$ , undergoes polymerisation to form the multi-ion polyphosphate. Polymerisation is allowed to continue till a product of optimum chain length is formed as determined by its chemical properties. This polyphosphate product is a viscous, acidic liquid. When neutralised with magnesia or ammonia, in the presence of water, a light coloured suspension is formed which can be dried and ground to a free flowing, non-hygroscopic product.

#### **Iron-manganese fertilizer**

The starting materials are yellow oxide of iron, i.e., goethite which may contain up to 62.8% Fe, pyrolusite which may contain upto 63% Mn, magnesia which may contain up to 60.3 % Mg and phosphoric acid containing not more than 60%  $\text{P}_2\text{O}_5$ . The raw materials, goethite and pyrolusite, are in such proportions that Fe : Mn = 2 : 1 (w : w). Although higher or lower ratios may be used, this ratio of 2 : 1 is most suitable from the point of view of crop requirements. Magnesia is added in the proportion Fe : Mg (weight ratio) = 2 : 1. With lower ratios of Mg, desirable properties are not obtained, higher ratios of Mg does not result in any particular



improvement of the product or the process. Therefore, a Fe : Mg ratio of 2 : 1 is optimum. The amount of phosphoric acid added is such that all the Fe, Mn and Mg in the reaction mixture are converted to the dihydrogen phosphates. Therefore, the Fe : Mn : Mg : P weight ratio is 2 : 1 : 1 : 8.1. Lower ratios of P will result in incomplete reaction of the oxides. Higher levels of P are of no particular advantage. On the contrary, this will result in excess acidity in the product that will require more base for neutralisation.

The reactants are taken in a glass vessel and heated over a hot plate at 150°C. Stainless steel cannot be used since Mn<sup>4+</sup> is a strong oxidising agent and will attack steel. Alternatively, acid-proof brick lined vessels may also be used. Temperature of heating should not exceed 170°C as polymerisation of iron phosphates will begin before pyrolusite dissolves resulting in undesirable products. Temperatures less than 100°C will cause very slow reaction and require very long periods of heating.

After the formation of dihydrogen phosphates, in the form of thick slurry, the reaction temperature is raised to 200°C for polymerisation to occur. Any temperature above 170°C can be used. At above 250°C, a homogenised product is not obtained since iron phosphates begin to polymerise before the pyrolusite can dissolve. Optimum reaction temperature is at 200°C. Heating is continued for 50 min at 200°C. The product is tested by taking a small portion, neutralising with MgO to pH 7.5 and testing its solubility in 0.33M citric acid and 0.005M DTPA (diethylene triamine penta acetic acid). The product of desired degree of polymerisation dissolves in these reagents within 30 min. Higher polymerised product will leave an insoluble residue and is not a desirable material. Lower polymerised products may contain unreacted black particles (pyrolusite).

The polyphosphate is a flowable liquid when hot but when cooled to room temperature, it becomes a thick, highly viscous material. A suspension of magnesia in water is added to this polyphosphate and it is stirred. Addition of magnesia is continued till the pH of the suspension is raised to 7.5. About 300 g MgO is required for the product from 100g goethite.

After neutralisation, the dark blackish product changes colour to a light grey material. This is dried in an oven at about 80°C then ground in a mortar and passed through 100 mesh sieve.

The principle underlying the production of bio-release iron-manganese fertilizer according to the process of the present invention is that when goethite, pyrolusite and magnesia are heated with phosphoric acid, the dihydrogen phosphates, viz.,  $\text{Fe}(\text{H}_2\text{PO}_4)_2$ ,  $\text{Mn}(\text{H}_2\text{PO}_4)_2$  and

$\text{Mg}(\text{H}_2\text{PO}_4)_2$  are formed and water is eliminated. For the reaction to proceed towards the formation of dihydrogen phosphates, the water formed during reaction must be removed by heating. Magnesia reacts most readily with the acid followed by goethite. Pyrolusite is much more resistant to dissolution in phosphoric acid. Whereas lower temperatures (around  $100^\circ\text{C}$ ) are sufficient to dissolve magnesia and goethite, the dissolution of pyrolusite requires much higher temperatures. However, the initial digestion temperatures cannot be allowed to exceed  $170^\circ\text{C}$  since iron phosphates will start to polymerise before pyrolusite has substantially dissolved. Once a fairly homogenous slurry is formed, it is heated to polymerisation temperatures. Polymerisation occurs by the formation of  $-\text{P}-\text{O}-\text{P}-$  linkages between adjacent phosphate groups. A linear chain is, thus, formed with  $\text{Fe}^{3+}$ ,  $\text{Mn}^{4+}$  and  $\text{Mg}^{2+}$  being linked to the remaining O atoms on the P. Ions like  $\text{Fe}^{3+}$  having multiple charges can cause extensive cross-linking of chains leading to a 3-D structure from which the  $\text{Fe}^{3+}$  or  $\text{Mn}^{4+}$  cannot be extracted even by complexants.  $\text{Fe}^{3+}$  by itself forms highly insoluble polyphosphates even at low degrees of polymerisation. On the contrary,  $\text{Mn}^{4+}$  forms polyphosphates with high solubility even in water. Therefore, combining  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  into one compound provides a balancing effect on their extreme solubility characteristics. Addition of  $\text{Mg}^{2+}$  further improves the solubility characteristics by weakening the strength of the cross linkages and making the compound more soluble in complexants.

Polymerisation must be stopped before the product becomes much too insoluble in complexants, since this would reduce availability of the nutrients to plants. The polyphosphate contains acidic  $\text{P}-\text{OH}$  groups; moreover, it is in a semi-liquid form. To convert the compound to a dry solid, the acidic  $\text{P}-\text{OH}$  groups have to be neutralised.  $\text{MgO}$  is a good neutralising agent;  $\text{NH}_3$  can also be used, but the product has higher water solubility than the  $\text{MgO}$  neutralised product.

This invention provides a process for the production of a new type of slow-release fertilizer, viz, bio-release fertilizers. All existing slow-releasing fertilizers of the micronutrients have nutrient release controlled by hydrolysis or diffusion mechanisms. The new bio-release forms have a superior nutrient supply mechanism, which is similar to that from the soil nutrient storehouse. Thus, this is the only Fe-Mn fertilizer wherein the nutrients are present in water insoluble but simultaneously in a plant available form. This invention also provides a substantial improvement in the existing process of production of water insoluble iron and manganese fertilizers. Unlike as in glass frits, much lower temperatures are required for production


Accordingly, this invention provides a process for the production of bio-release iron-manganese fertilizers. These fertilizers have low solubility in water but the nutrients are in a form that is available for plant uptake. The fertilizers are also non-toxic, non-hygroscopic, easy to apply and exhibit improved fertilizer use-efficiency. The main advantage of this process is the improvement in product properties and process control, by combining iron, manganese and magnesium. Iron or manganese alone or in combination would not give products of desirable solubility properties. By introducing Mg into the structure the product is far superior.

Various modifications are within our investigation. Thus, the four components need not be added one after the other to form a total mass for reaction.

These may be added in group of two or more, reaction carried out and incremental addition may also be possible.

We are also investigating alternate reactions and reaction patterns and neutralizing agents where needed.

Dated this 31st day of July, 2003

  
( K. RAJAGOPALAN )  
OF RAJAGOPALAN & ASSOCIATES  
AGENT FOR THE APPLICANTS

05 AUG 2004

THE PATENT ACT, 1970

COMPLETE

# SPECIFICATION

(SECTION - 10)

## TITLE

"A PROCESS FOR THE MANUFACTURE OF BIO-RELEASE  
IRON-MANGANESE FERTILISER "

## APPLICANT

DEPARTMENT OF SCIENCE & TECHNOLOGY (DST),  
TECHNOLOGY BHAWAN, NEW MEHRAULI ROAD,  
NEW DELHI - 110 016, INDIA.  
AN INDIAN GOVERNMENT ORGANIZATION.

ORIGINAL

The following specification particularly describes and ascertains the  
nature of this invention and the manner in which it is to be performed.

## **Field of invention**

This invention relates to a process for the manufacture of bio-release types of slow-release iron-manganese fertilizer compounds wherein these micronutrients are water insoluble but are nevertheless available for plants.

## **Background of invention : Prior Art And Drawbacks**

Iron and manganese fertilizers are widely used in many parts of the world particularly in soils of high pH, such as the black soils. They are also widely used in horticultural and cash crops to improve yields and quality of produce. The compounds most popularly used for correcting deficiencies of iron and manganese in crops are ferrous sulphate and manganous sulphate (J.J. Mortvedt, P.M. Giordano & W.L. Lindsay, 1972, Micronutrients in Agriculture, Soil Sci. Soc. Am., Madison). Chelated forms of these micronutrients, e.g., iron-EDTA, and manganese -EDTA compounds are also in use as liquid sprays (V. Saucheli, 1967, Chemistry and technology of fertilizers, Reinhold, New York; G.H. Collins, 1955, Commercial fertilizers, Mc-Graw Hill, New York).

There are, however, several drawbacks in the use of such soluble compounds as fertilizers of iron and manganese, e.g., leaching losses, chemical transformation losses, ground water contamination, etc. This results in excess dosages which are often several times the actual crop uptake, leading to poor fertilize-use efficiency.

Moreover, such wastages also affect the economics of iron and manganese fertilizer, thereby discouraging their widespread usage.

In an attempt to overcome these shortcomings, slow-release fertilizers incorporating iron and manganese have been prepared. One such type is the fertilizer based on phosphate glasses known as frits. Frits are prepared by fusing sodium, potassium or ammonium dihydrogen phosphates together with micronutrient salts at temperatures between  $800^{\circ}$  and  $1400^{\circ}\text{C}$  and then rapidly quenching the melt to produce a glass (G.J. Roberts 1973, Am. Ceram. Soc. Bull. Vol 52, p383; *ibid*, *idem*, Vol 54, p1069; Austrian Patent No 326160 of 1975; US Patent No. 3574591 of 1971; US Patent No 2713536 of 1974).

The major disadvantage of the phosphate glass frits is that the availability of the nutrients is by slow hydrolysis of the glass and is highly dependent on the soil (pH, moisture content, temperature, etc.,) and on the crop (rate of growth, physiological factors, variety, etc). Consequently, where nutrient release by hydrolysis does not match plant uptake, the fertilizer is not effective. Moreover, the high temperatures involved in the synthesis of frits together with the corrosive conditions make these materials fairly expensive and unsuitable for general use.

Another type of phosphate based water insoluble fertilizer is the metaphosphate. Metaphosphates of calcium and potassium together with micronutrients have been proposed (SI Volfkovich, 1972, J Appl. Chem. (USSR) Vol 45, p2479); A Russian

patent (SU 1270148 of 1986) describes the production of mixed metaphosphates based fertilizers produced at  $500^{\circ}$ - $880^{\circ}$ C. Drawbacks in the use of metaphosphates as fertilizers are similar to those with the frits. Metaphosphates may be more insoluble and hydrolyse even slower, producing compounds with very poor nutrient availability. Metaphosphates of the heavy metals are extremely insoluble and of little use as fertilizers.

An additional type of slow-release fertilizer has been produced in which the micronutrient ions are in a chemical form wherein they are insoluble but also plant available. These belong to the bio-release types of slow-release fertilizers. The processes for producing such phosphate based zinc and copper fertilizers are described in two Indian patents (Nos 172800 of 1990 and 177205 of 1991). The chemistry of zinc and copper phosphate polymerisation and the chemical nature of these fertilizers have also been described (SK Ray, C Varadachari & K Ghosh, 1993, Ind. Eng. Chem. Res. Vol. 32, p. 1218; SK Ray, C Varadachari & K Ghosh, 1997, J. Agric. Food Chem., vol. 45, p. 1447). A new patent (C. Varadachari, Indian Patent Application No. 10/CAL/99) describes the processes for production of slow-release fertilizers and describes methods for assessing limits of polymerisation.

4.

### **Objectives of the invention**

An objective of this invention is to propose a process for the manufacture of bio-release iron-manganese fertilizer having all the advantages of slow-release fertilizers together with the added benefit of high nutrient availability.

Another objective of this invention is to provide a combined nutrient source of iron and manganese in a single compound. Since deficiencies of iron and manganese in soils always occur together, therefore, a fertilizer providing both nutrients would be more beneficial for crop growth.

The third objective of this invention is to provide a bio-release source of ammonium, magnesium and phosphorus, all of which are essential plant nutrients.

Still another objective of this invention is to propose a process for the manufacture of bio-release iron-manganese fertilizer, wherein only a single heating stage is required and polymerisation temperatures are lower than all previous processes.

Yet another objective of the invention is to provide a processes for producing slow-releasing, water insoluble, iron-manganese fertilizers that will show good bio-availability of the nutrients and thus provide an effective source of iron and manganese for plants.



A further objective is to provide processes, which offer substantial improvements over earlier processes, in providing a combined micronutrient source and also in terms of energy requirement

### **Description of the invention**

According to this invention, there is provided a process for the preparation of water insoluble bio-release iron-manganese fertilizer, which comprises (a) heating phosphoric acid with a mixture of (i) source of iron oxide such as goethite and hematite, (ii) pyrolusite and (iii) one or more basic compound(s) selected from oxide(s) or carbonate(s) of magnesium, calcium, sodium and potassium, (b) neutralisation followed by drying and pulverisation.

When oxide of iron [goethite i.e.,  $\text{FeO}(\text{OH})$  or hematite i.e.,  $\text{Fe}_2\text{O}_3$  ], pyrolusite ( $\text{MnO}_2$ ) and a basic compound (oxides or carbonates of magnesium, calcium, sodium or potassium) are heated with phosphoric acid, reaction occurs to form the dihydrogen phosphates of the metal ions, which subsequently polymerise to form iron manganese polyphosphate.

Removal of free water from the system by heating facilitates the reactions.

Vacuum facilitates the reaction by speeding up the removal of water.

Polymerisation is allowed to continue till a product of optimum chain length is formed as determined by its chemical properties. This polyphosphate product is a

viscous, acidic liquid. When neutralised with magnesia or ammonia, a light coloured suspension is formed which can be dried and ground to a free flowing, non-hygroscopic product.

### **Iron-manganese fertilizer**

The starting materials are yellow oxide of iron, i.e., goethite, which may contain up to 62.8% Fe or red oxide of iron, i.e., hematite containing up to 69.9 % Fe. pyrolusite which may contain up to 63% Mn, magnesia which may contain up to 60.3 % Mg or magnesium carbonate which may contain up to 28.8 % Mg and phosphoric acid containing not more than 60%  $P_2O_5$ .

The raw materials, goethite and pyrolusite, are in such proportions that molar ratios of Fe : Mn = 1 : 0.51. Although higher or lower ratios ranging from Fe : Mn = 1 : 0 to 0 : 1 may be used, this ratio of 1 : 0.51 is considered most suitable from the point of view of crop requirements. Magnesia is added in the proportion Fe : Mg (molar ratio) = 1 : 1.15.

With lower ratios of Mg, desirable properties are not obtained; higher ratios of Mg do not result in any particular improvement of the product or the process. Product remains tolerable with Fe: Mg molar ratios ranging from 1 : 0.6 to 1 : 1.75. However, a Fe : Mg molar ratio = 1 : 1.15 is optimum. The Mg compound may also be replaced with a Ca compound. Thus dolomite ( $CaCO_3 \cdot MgCO_3$ ) or

limestone ( $\text{CaCO}_3$ ) may be used. The molar proportion of Fe : cation is preferably 1 : 1.15 although ratios ranging from 1 : 0.575 to 1 : 1.725 may also be used. Alternatively, sodium or potassium bases may be used. In such case, the Mg is replaced by equivalent amounts of Na or K.

The molar ratio of Fe : Na/K = 1 : 2.3 is at the optimum level. The amount of phosphoric acid added is such that all the Fe, Mn and Mg as well as impurities in the reaction mixture are converted to the dihydrogen phosphates. Thus, the Fe : Mn : Mg : P molar ratios used are 1 : 0.51 : 1.15 : 7.34. Lower ratios of P will result in incomplete reaction of the oxides. Higher levels of P at any level may be used but is of no particular advantage. On the contrary, this will result in excess acidity in the product that will require more bases for neutralisation.

The reactants are taken in an acid-proof brick lined reactor vessel. All the reactants are mixed together and heated at  $200^\circ\text{C}$ . Application of vacuum at this stage facilitates the reaction. As the reaction progresses, the colour changes from dirty yellow or red (depending on the colour of the starting material): it deepens and ultimately becomes almost black. Any temperature above  $160^\circ\text{C}$  can be used for the reaction; however, temperatures of  $200\text{--}250^\circ\text{C}$  give the optimum results. Temperature of liquid itself, however, remains at around  $140^\circ\text{C}$ . Pre-heating at lower temperatures is not required since dissolution of solids occurs during the period when liquid temperature slowly increases by absorption of external heat. As

the system absorbs heat, initially, dihydrogenphosphates of iron, manganese and magnesium are formed. With further absorption of heat, polymerisation of the phosphates occurs with formation of iron manganese magnesium polyphosphate. By eliminating the initial heating period, the reaction is much faster without any loss of product quality. The reaction can be followed by observing the changes in colour, density and viscosity of the liquid. At the end of the reaction period the liquid is almost black in colour. Density changes are also useful to obtain the end-point of reaction. Density of the liquid shows a sharp increase near the end-point; it is 1.97 g/ml (in the hot state, at around  $140^{\circ}\text{C}$ ) in the product having the desired polymerisation. Viscosity changes are also sharp; viscosity increases from around 19 centipoise to 43 centipoise (at a temperature of about  $140^{\circ}\text{C}$ ) at the end-point. The polyphosphate is a flowable liquid when hot but when cooled to room temperature, it becomes a thick, highly viscous material. After the end-point of reaction, if heating is further continued, the liquid becomes highly viscous and hair-like strands are formed, which solidify on cooling.

Further testing of the product is done by taking a small portion, neutralising with ammonia to pH 5.0-7.5. Optimum pH for neutralisation is pH 5.6-6.0. The product is tested for its solubility in 0.33M citric acid and 0.005M DTPA (diethylene triamine penta acetic acid). The product of desired degree of polymerisation is almost completely soluble in these reagents within 60 min.

-9-

Higher polymerised product will leave an insoluble residue and is not a desirable material. Lower polymerised products may contain unreacted black particles (pyrolusite).

The polyphosphate, at the desired level of polymerisation, is a flowable liquid. It is poured into a container, allowed to cool to room temperature and subsequently neutralised with a basic material. Ammonia solution is preferred because time requirement for neutralisation reaction is faster compared to solid bases like magnesia, magnesium carbonate, lime, etc. However, any such basic material may be used. Optimum pH for neutralisation is 5.5- 6.5. If too little base is added, the finished product will tend to become hygroscopic. Solubility in citrate and DTPA solutions will also be lower. Addition of too much of base offers no particular advantage and will also make the product more insoluble in citrate and DTPA solutions. After neutralisation, the dark blackish product changes colour to a light gray material. This is dried at temperatures  $< 100^{\circ}\text{C}$ , preferably at  $60-80^{\circ}\text{C}$ . It is then ground and sieved, preferably through 100 mesh.

This invention provides a substantial improvement over previous processes for the production of combined iron-manganese fertilizers. In this process the initial reaction stage to produce a homogenous mixture is eliminated. A single stage reaction, at temperatures of  $160^{\circ}\text{C}$  or higher is sufficient to produce the polyphosphate. Thereby total time of reaction is reduced. This has been possible

because of addition of  $Mg^{2+}$  ions, which helps in more rapid and easier dissolution of pyrolusite. The polymerised end product remains in a liquid state, which makes material handling and transfer easier. Process control is also simplified since density and viscosity of the liquid can be continuously monitored and thereby the end-point of reaction can be readily detected.

Accordingly, this invention provides a process for the production of multinutrient bio-release fertilizer of iron-manganese. All existing slow-releasing fertilizers of the micronutrients have nutrient release controlled by hydrolysis or diffusion mechanisms. The new bio-release forms have a superior nutrient supply mechanism, which is similar to that from the soil nutrient storehouse. Thus, in this Fe-Mn fertilizer the nutrients are present in water insoluble but simultaneously in a plant available form. The fertilizers are also non-toxic, non-hygroscopic, environment friendly, easy to apply and exhibit improved fertilizer use-efficiency.

The main advantage of this process is the significant improvement in energy use by converting a two-stage process to a single stage process. Another advantage is improvement in process control, by combining iron, manganese and magnesium, which produces liquid polyphosphates whose solubility characteristics are less sensitive to the degree of polymerisation. This is more difficult in iron-manganese systems in the absence of magnesium. Yet another advantage of this invention is the easy technique of obtaining the end-point of reaction by continually monitoring

11.

density or viscosity of the liquid. Lastly, the process is simpler and requires less energy inputs than all previous processes.

The invention will now be explained in greater detail with the help of the following non-limiting examples.

### Example 1

Phosphoric acid containing 60 %  $P_2O_5$  is taken in a glass beaker. To 145 g of the acid, 16 g of goethite (containing 62 % Fe), 7.86 g pyrolusite (containing 63 % Mn) and 8.2 g magnesia (containing 60.3 % Mg) is added and stirred. The colour of the mixture at this stage is dirty yellow. The beaker is then placed in a furnace set at  $200^{\circ}C$ . Much frothing occurs as the polymerisation proceeds. After 45 min of heating, the beaker is taken out of the furnace. At this stage the colour of the liquid is almost black. A small amount is taken for density and viscosity measurements of the hot liquid. These values are about 1.97 g/ml and 43 centipoise respectively. Another portion is neutralised with ammonia to pH 5.6 and tested for its solubility in 0.33M citric acid. The desired product gives an almost clear solution within 60 min. Materials, which are much too polymerised or too little polymerised leave a residue.

The polyphosphate, when hot, is a flowable liquid. It is allowed to cool to room temperature whereupon it becomes a viscous liquid. 85g of magnesium oxide is

added to the polyphosphate with mixing. The pH of the product is, thus, raised to about 5.6. Its colour changes to very light gray. It is then dried in an oven at  $80^{\circ}\text{C}$ , ground in a mortar and sieved with 100 mesh sieve. The fertilizer contains 5.4%  $\text{Fe}_2\text{O}_3$ , 2.7%  $\text{MnO}_2$ , 18.4%  $\text{MgO}$  and 34.5%  $\text{P}_2\text{O}_5$ .

### Example 2

12 kg of commercial phosphoric acid containing 58.5%  $\text{P}_2\text{O}_5$  is taken in an acid-proof brick lined reactor vessel with a stirrer. To this, 732 g pyrolusite (containing 51.6% Mn), 1212g goethite (containing 62% Fe) and 1836g magnesium carbonate (containing 20.5% Mg) are added, one after another. It suspension is stirred. Frothing occurs due to the presence of carbonate. The vessel is closed, stirring is continued and heating is started with the temperature set at  $200^{\circ}\text{C}$ . Density and viscosity of the liquid are continuously recorded and heating is stopped as the appropriate stage is reached (density of 1.97g/ml and viscosity of around 43 centipoise). For this quantity of reactants 90 min heating is required at  $200^{\circ}\text{C}$ . The liquid is poured out into a stirrer. It is allowed to cool to nearly room temperature then 11 litre ammonia solution (25% ammonia) is slowly added with continuous stirring. A sample is taken and tested for its pH, which should be around 5.6-6.0. The suspension is poured out into trays and dried in an oven at  $80^{\circ}\text{C}$ . It is finally ground to a 100 mesh size.



The fertilizer contains 5.5 % Fe, 2.8 % Mn, 16 % P, 3 % Mg and 11 % N. It is tested to be almost completely soluble in 0.33M citric acid and 0.005M DTPA.

Plant growth trials with this fertilizer were done in black cotton soil with rice, spinach and chillies as test crops. Rice produced a 45% increase at 2 kg/ha Fe and 1 kg/ha Mn as the bio-release fertilizer. Chillies gave a 179% higher yield at the same dose of bio-release fertilizer. The residual effect of the fertilizer produced a 51% increase in yield of spinach.

### Example 3

135 g commercial phosphoric acid (containing 58.5 %  $P_2O_5$ ) is mixed with 16g hematite (containing 50.5 % Fe and 2.87 % Al), 7.84g pyrolusite (containing 51.6 % Mn) and 19.7g magnesium carbonate (containing 20.5 % Mg). The reactants are taken in a borosilicate glass beaker, stirred and kept in a muffle furnace set at  $250^{\circ}C$ . After 20 min the beaker is removed from the furnace. A sample is neutralised with ammonia up to a pH of 5.6 and its solubility in 0.33 M citric acid is tested. It is almost completely soluble. A light gray product is formed which is dried at  $70^{\circ}C$  in an oven. The dried material was powdered and sieved through 100 mesh.

**Example 4**

This procedure is essentially the same as described in example 1 except in the order of addition of reactants. Here phosphoric acid is taken in a beaker, pyrolusite is added to it and the mixture is heated at  $200^{\circ}\text{C}$  for 10 min. The beaker is removed from the furnace and goethite and magnesium are added with stirring. The reactants are again heated at  $200^{\circ}\text{C}$  for 30 min. The end product is tested as described in example 1; the finished product is also obtained as described therein.

**Example 5**

This is essentially the same as example 2 except that at the neutralisation stage, 11 kg potassium carbonate is used instead of ammonia solution.

**Example 6**

This is essentially the same as example 1 except that at the initial reaction stage dolomite 22.5g (containing 21% Ca and 13% Mg) is added as an ingredient, instead of magnesium carbonate. The mixture is heated at  $250^{\circ}\text{C}$  for 40 min to obtain the desired level of polymerisation.

**Example 7**

This is essentially the same as example 1 except that at the initial reaction stage 31.8g sodium carbonate (containing 29 % Na) is used instead of magnesium carbonate. The mixture is heated at 250°C for 100 min to obtain the desired level of polymerisation.

**Example 8**

This is essentially the same as example 1 except that 8g sodium hydroxide (containing 57.5% Na) is used instead of magnesium carbonate.

**Example 9**

This is essentially the same as example 1 except that 90g magnesium carbonate (containing 28 % Mg) is used for neutralisation instead of ammonia.

**Example 10**

This is essentially the same as example 1 except that at the initial reaction stage calcium carbonate 20.7 g (containing 40 % Ca) is added as an ingredient, instead of magnesium carbonate. The mixture is heated at 250°C for 50 min to obtain the desired level of polymerisation.

**We Claim :**

1. A process for the preparation of water insoluble, bio-release iron- manganese fertilizer which comprises,
  - (a) heating phosphoric acid with a mixture of (i) source of iron oxide such as goethite and hematite, (ii) pyrolusite and (iii) one or more basic compound(s) selected from oxide(s) or carbonate(s) of magnesium, calcium, sodium and potassium,
  - (b) neutralisation followed by drying and pulverisation.
2. A process as claimed in Claim 1 wherein the iron oxide and pyrolusite are used in any of the molar ratios of  $\text{Fe} : \text{Mn} = 1 : 0$  to  $0 : 1$ .
3. A process as claimed in Claims 1 and 2 wherein the iron oxide and pyrolusite are preferably used in the molar ratio of  $\text{Fe} : \text{Mn} = 1 : 0.51$ .
4. A process as claimed in Claim 1 wherein the basic compound is preferably magnesium oxide or carbonate and is used in the molar ratio of  $\text{Fe} : \text{Mg} = 1 : 0.6$  to  $1 : 1.75$  but preferably in the ratio  $1 : 1.15$ .
5. A process as claimed in Claim 1 wherein the basic compound is calcium oxide or carbonate and is used in the molar ratio of  $\text{Fe} : \text{Ca} = 1 : 0.6$  to  $1 : 1.75$  but preferably is  $1 : 1.15$ .

6. A process as claimed in Claim 1 wherein the basic compound is potassium oxide or carbonate and is used in the molar ratio of Fe : K = 1 : 1.2 to 1 : 3.5 but preferably is 1 : 2.3.
7. A process as claimed in Claim 1 wherein the basic compound is sodium oxide or carbonate and is used in the molar ratio of Fe : Na = 1 : 1.2 to 1 : 3.5 but preferably is 1 : 2.3.
8. A process as claimed in Claims 1 to 7 where phosphoric acid is used is equal to or greater than that required to convert all the cations in the reaction mixture to dihydrogen phosphates.
9. A process as claimed in Claims 1 to 8 where the components Fe, Mn, Mg or Ca and P are preferably used in the molar ratio of Fe : Mn : Mg or Ca : P = 1 : 0.51 : 1.15 : 7.34.
10. A process as claimed in Claims 1 to 8 where the components Fe, Mn, K or Na and P are preferably used in the molar ratio of Fe : Mn : K or Na : P = 1 : 0.51 : 2.3 : 7.34.
11. A process as claimed in Claim 1 wherein the reaction is carried out at any temperature of 160°C and above.
12. A process as claimed in Claim 1 wherein the reaction is preferably carried out in the temperature range of 200-250°C.

13. A process as claimed in Claim 1 to 12 wherein water formed during the initial reactions is removed by heating or vacuum.
14. A process as claimed in Claim 1 to 13 wherein the reaction is terminated on the partial polymerisation of the polyphosphate as herein exemplified.
15. A process as claimed in Claim 1 wherein the liquid product is neutralised with a base and dried at a temperature not exceeding  $100^{\circ}\text{C}$ , optimally at  $60-80^{\circ}\text{C}$ .
16. A process as claimed in Claim 1(b) wherein the base for neutralisation is selected from magnesia, magnesium carbonate, lime and ammonia and is preferably ammonia.
17. A process for the preparation of water insoluble iron-manganese fertilizers substantially as herein described with reference to the examples.

DATED THIS THE ~~Four~~ DAY OF AUGUST 2004.



( K.RAJAGOPALAN).

( RAJAGOPALAN AND ASSOCIATES)

( AGENT FOR APPLICANT).

05 AUG 2004

**A B S T R A C T**

This invention provides a process for the preparation of water insoluble, bio-release iron-manganese fertilizer which comprises, heating phosphoric acid with a mixture of (i) source of iron oxide such as goethite and hematite, (ii) pyrolusite and (iii) one or more basic compound(s) selected from oxide(s) or carbonate(s) of magnesium, calcium, sodium and potassium, (b) neutralisation followed by drying and pulverisation.

ORIGINAL

**THIS PAGE BLANK (USPTO)**

**PCT/IN2004/000234**





**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☒ **FADED TEXT OR DRAWING**

☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☒ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**